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Temperature Dependence of Hydrolysis of Polyimide Wire Insulation

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Degradation of polymeric materials as a chemical reaction rate related to exposure temperature has been confirmed by many laboratory studies and the rate equation, enhanced by other stresses and environmental conditions, has been utilized to compare the service life expectancy of various electrical insulation materials and systems for many years. In recent Naval aircraft wiring applications it has been experienced that a

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20. ABSTRACT (Continued)

popular polyimide insulation undergoes degradation by a hydrolytic chain splitting reaction that can be attributed to an unexpected number of service failures. In this initial study it has been determined that the reaction does proceed in a neutral pH aqueous environment at a rate that is temperature dependent, and the data of life versus temperature conforms to an Arrhenius plot so that from accelerated tests at elevated temperatures it is possible to extrapolate to service temperatures. Continuing studies will lead to the development of a functional aging procedure for applying a moisture exposure step into each cycle in order to more nearly predict service life of this insulation system and provide a comparison with other candidate systems.

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TEMPERATURE DEPENDENCE OF HYDROLYSIS OF POLYIMIDE WIRE INSULATION

INTRODUCTION

The number of Naval aircraft maintenance problems due to deteriorated wire insulation has increased at an appalling rate in the past few years. The wiring that was initially specified for general installation was selected for its expected durability along with its low weight and bulk characteristics. However, the inherent weakness of this insulating material, that of susceptibility to hydrolytic degradation which reduces the polymer chain length and renders the initially very strong material to a weak and brittle wire coating, was overlooked in the performance specifications. Therefore, many of the Navy's aircraft are wired with this polyimide type insulation that has become a major maintenance problem.

When cracking and fraying were initially observed the deterioration was attributed to the wires coming into contact with the high pH cleaning solutions used frequently on the aircraft. A study conducted at the Naval Air Rework Facility (NARF) North Island, CA[1] in 1976 demonstrated that the time for cracking to develop in polyimide wire insulations was a function of the pH and the temperature. In 1978, another study conducted at the Naval Air Development Center, Warminster, PA[2] demonstrated that even in distilled water (pH 7) the deterioration of polyimide insulation takes place, and it is more rapid at 75°C than at room temperature. Upon additional search for information on the observance of degradation of polyimide insulation it was found that failures occurred during storage of aerospace wiring in which the insulation is applied as a bonded Kapton® film on flat wire missile cables[3]. The failure was attributed to the high humidity of the uncontrolled environment in the cable stock room prior to the missile assembly. In other studies conducted at Grumman Aerospace in 1971[4] it was also concluded that the

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degradation of Kapton® polyimide film in aqueous media is due to a hydrolytic chain scission mechanism occurring at amide linkages present in the polyimide. Therefore, the previous studies provided the evidence that water in any form will attack the polyimide chain and produce degradation. Increasing the temperature of the exposures showed that the deterioration was accelerated so it was presumed feasible to apply the Arrhenius rate equation to a study of Kapton® insulated wire, especially since water is a component of the aging environment.

BACKGROUND

A program to study the thermal aging characteristics of wire insulation systems of interest to the Defense Department was initiated at the Naval Research Laboratory in 1958, sponsored initially by the Electronic Technology Laboratory of the Wright Air Development Division, United States Air Force, and subsequently by the Airborne Equipment Division, Bureau of Naval Weapons Department of the Navy. The program was continuous until about 1966. The results of this program demonstrated that the relationship between reliable life and the aging temperature of many commonly used power and hook-up wires in aircraft and missile systems could be determined[5]. By applying the laws of physical chemistry to the philosophy of functional evaluation, a standard procedure was adopted to obtain experimental data which plotted graphically into the straight-line relationship commonly known as the Arrhenius Plot. From experimental investigations of many different types of insulated wires, curves have been derived showing the utility of this procedure as a thermal-aging classifying system[5].

A very similar study was later started at the Lockheed Aircraft Corporation to compare results obtained by the Navy and to evaluate several new wire insulation systems that had more recently evolved. This work was reported by Elliot in 1972 with Arrhenius plots very similar to those previously derived from a similar functional aging procedure[6]. As a result of the two studies the ASTM Subcommittee on Hook-up Wire Insulation, D09.16 developed a standardized procedure, utilizing a compromise of the procedures of the above two studies, which is now published as a Standard Method of Testing Hookup Wire Insulation for Relative Thermal Life and Temperature Index[7].

The resulting life versus temperature relationships derived from these procedures are providing aerospace design engineers with information to select the wire insulation and to utilize minimum wire sizes required to maintain maximum reliability while reducing weight and bulk to a minimum. These procedures are based on the recognition that degradation is the result of a chemical reaction such as oxidation that occurs at a rate that is temperature dependent. This reaction then weakens the materials resistance to mechanical stress, moisture penetration and electrical stress which ultimately produce system failures.

Since this degradation is the result of a chemical reaction, the rate can be expressed by a mathematical formula derived from a combination of the first-order kinetic equation and the Arrhenius equation, which relates the thermodynamic equilibrium constant of a reacting process to the exposure temperature[8]. This derivation in final form is expressed as follows:

$$\text{Log } L = \log A + B/T$$

where

L = hours of life to a specified end-point while aging at a temperature T

T = absolute or Kelvin scale temperature (°C + 273)

A and B = constants of the intercept and the slope, respectively, and are related to the entropy of the system and the activation energy of the degradation process

This equation yields a straight-line curve which is easily interpreted when plotted on semi-log graph paper which has been specially prepared to present the hours of life on a logarithmic scale as the ordinate and the aging temperature in degrees Celsius on the abscissa with a scale that has been graduated to the reciprocal of the corresponding absolute temperature.

The life at any temperature can then be predicted from only three or four experimental points by extrapolating the curve of the experimental data of life versus temperature following a regression analysis. The reliability of the prediction will then depend upon the accuracy of the equation constants selected to describe the curve. Since deterioration is a function of chemical changes occurring in the insulation material, extrapolations are limited to the temperature region in which there are no transitions either in the physical structure of the plastic, such as melting, or in the chemical mechanisms of deterioration, such as a change from free-radical chain scission to rapid oxidation or combustion.

In actual service conditions, the wire will experience other exposures and stresses besides heat which can also contribute to deterioration and failure of the insulation. These may be environmental such as humidity, moisture, cold, dust, chemicals, and radiation. There will also be mechanical and electrical stresses. The magnitude and number of these conditions to which a wire may be exposed will depend on the type of aircraft, the location of the wire, and the components of the circuit. To evaluate typical life by a laboratory procedure, a compromise of simulated conditions which could be readily reproduced was adopted and standardized. It was derived from

combining existing standards, information from published reports, and opinions from personal surveys into a system by which multiple specimens could be easily processed. This procedure, which was utilized in the earlier NRL study provided the functional aging cycle through the following steps: thermal degradation in an oven; mechanical flexing to amplify physical weakness when embrittlement occurs; exposure to a moisture-saturated atmosphere, which will seek out cracks and porosities in the materials caused by heating and flexing; and finally a voltage stress, which determines the electrical integrity of the wire insulation in the moist atmosphere. By applying these steps in repeated cycles, the life at each temperature was readily determined.

By subjecting each wire sample to this procedure, the resulting curves obtained presented a comparison of the merits of a particular wire with respect to others of its classification. By plotting curves of many wires on a single graph, it was found that within each MIL-specification, a range of typical characteristics could be outlined. From results of all tests conducted in that study, typical ranges of life versus temperature are presented graphically in Figure 1 for the following wire specifications: MIL-W-5086A, MIL-W-8777A, MIL-W-7139A, MIL-W-25038, MIL-W-16878C - "E" and "EE."[5] Specifying 10,000 hours as the rated operating life desired, the approximate normal operating temperatures which can be specified for these wires are listed in Table I. This information can be a very useful tool to the design engineer for selecting the type of wire needed for particular temperature zones and thermal load requirements.

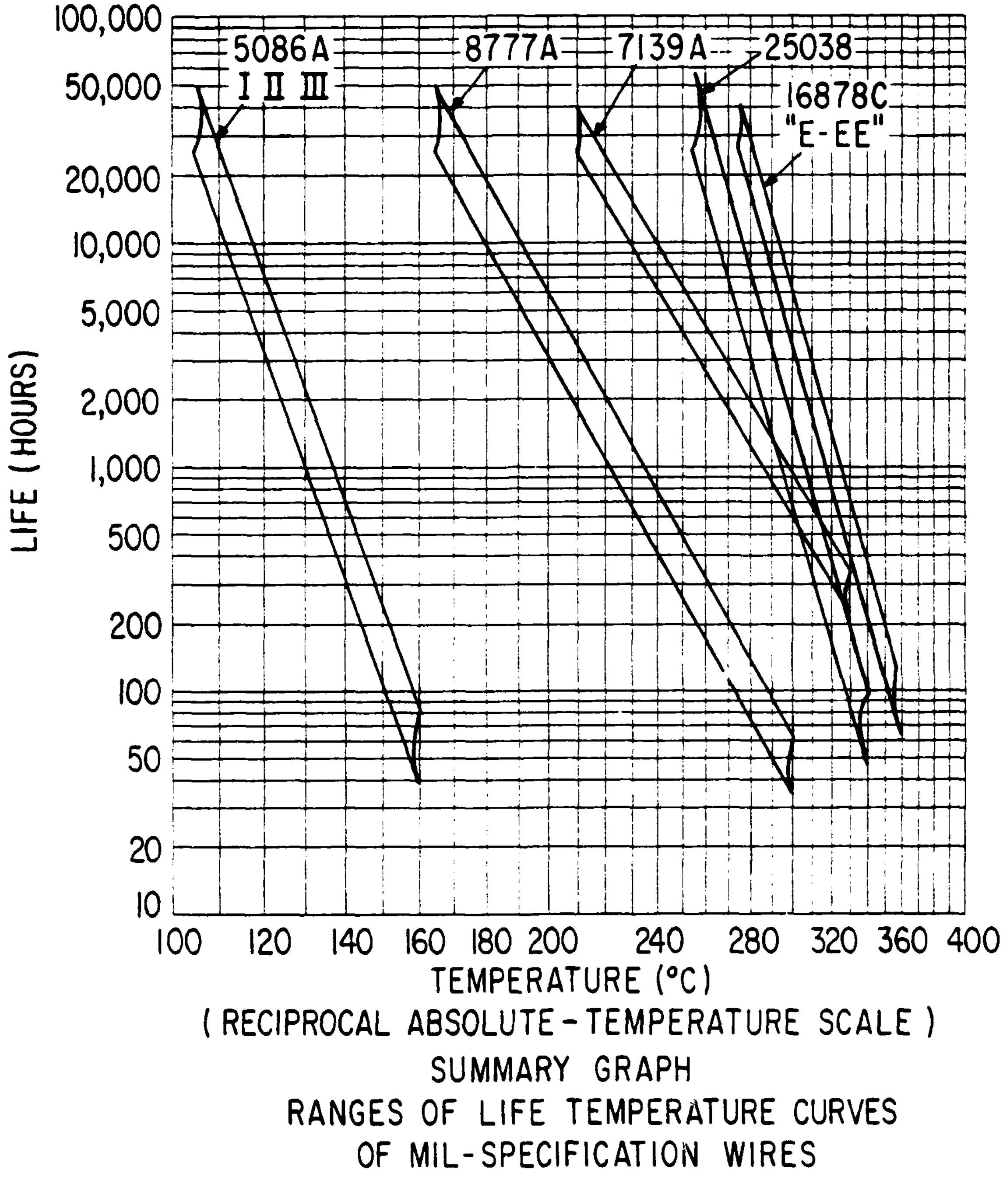

Figure 1. Summary graph of the Arrhenius plots of various aircraft wires showing the ranges of life-temperature curves for each type of insulation. (from Ref. 5)

Table I. Classifying temperatures of various types of aircraft wires derived from The Arrhenius plots of Figure 1.[5]

Military Specification	Average Classifying Temperature at 10,000 hours, °C
MIL-W-5086A	115
MIL-W-8777A	185
MIL-W-7139A	235
MIL-C-25038	270
MIL-W-16878C, types E and EE	290

Since the recent experiences with Kapton® insulated wires have found that hydrolytic degradation due to moisture and high pH fluid exposures is the primary cause of wiring failures, the current study has been directed toward the inclusion of such an environmental condition into a modification of the standard procedure described above. The initial experiments which were conducted to determine if the hydrolysis reaction also followed the Arrhenius rate will be described in the next section.

EXPERIMENTAL

Experiments were conducted to determine the temperature-life relationship of the hydrolytic degradation reaction under accelerated conditions. The procedure consisted of aging wire specimens in water at various temperatures and testing to determine the time to reach an arbitrary end-of-life, determined by a proof-voltage test.

The experimental apparatus consisted of three 3-liter reaction kettles filled with deionized water and fitted with heating mantles and water-cooled condenser tubes. Temperatures were controlled at 60°C, 80°C and 100°C with Versatherm® electronic temperature controllers linked to mercury contact thermo-regulators. With this system the water temperatures were controlled to within ± 1°C. A view of the controllers and kettles with wire specimens being aged is shown in Figure 2.

The pH of the water at room temperature was measured with a Fisher Acumet® pH meter. Initially, when the kettles were filled from the Barnstead 803 Demineralizer, the pH was 6.95. After completion of the aging exposures of the wires being studied the water from the 100°C kettle (after approximately three months) was again measured at room temperature and was found to have a pH of 8.60. No post-exposure measurements were made on the water from the other two kettles.

Specimens were prepared from samples of MIL-W-81381/11 wires obtained from the Defense Industrial Supply Center, representative of two different manufacturers. Each specimen consisted of a 32-inch length of wire wrapped tightly around a ½-inch diameter rod of TFE-Teflon® for a wrapped length of 10-inches, or 5½ turns. Waterproof FEP-Teflon® tape was employed to hold the wire in place on the rod throughout the exposure life of the specimen.

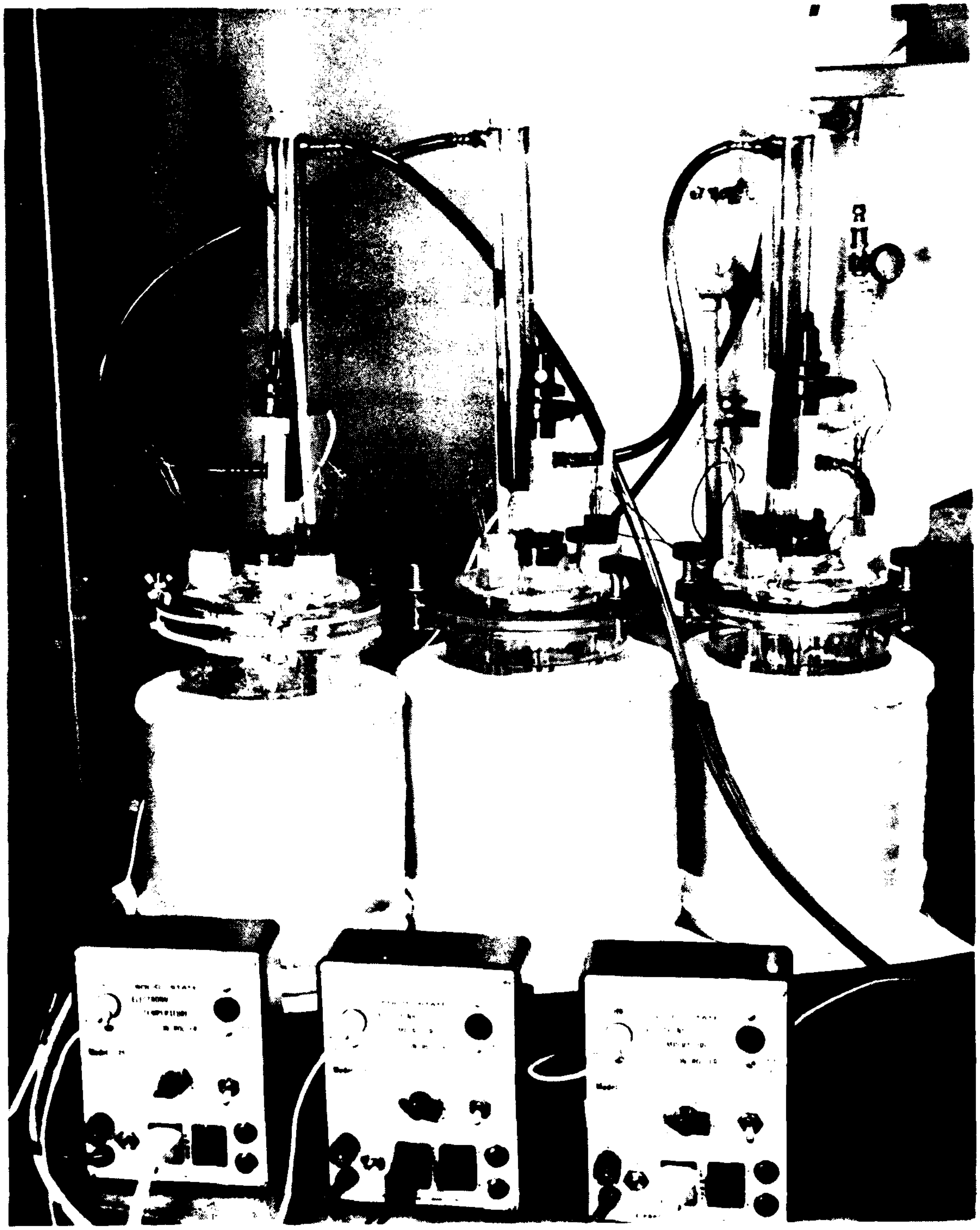

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Figure 2. Controlled temperature water immersion system for wire specimens.

The two ends of the wire were stripped and twisted together, giving a 10-inch straight wire handle to facilitate the immersion of the specimen into the hot water for aging and in the cold water of the voltage proof-test beaker.

After each hot water aging cycle the specimens were cooled in water at room temperature and then examined for cracks in the wire jackets. In most wire samples the appearance of cracks was a good indication that the proof-test failure was iminent. End-of-life was determined by applying a voltage stress of 2500 volts rms between the conductor and a ground wire in the beaker of tap waters for 30 seconds. With the Peschel Series H, Sensitive Hipot Tester, a voltage rise of one second per kilovolt was applied. Overload sensitivity was set at 500 μA, so that a failure occurred either on the complete breakdown at a point in the insulation or when leakage current of the degraded specimen exceeded this amount. A view of the test is shown in Figure 3. If failure did not occur the specimens were returned for another cycle of aging in the hot water.

A close-up of two wire specimens that had failed the proof-test is shown in Figure 4. Many cracks developed in the top coat of the wires during the water aging, and it was usually noticed before the specimen aged to the failure cycle, giving a warning of the approach of the failure time. When voltage breakdown did occur, it was through the primary insulation at one of these cracks. The number of cracks developing differed with each manufacturer's wire, indicating that variations are permissible in the top-coating process.

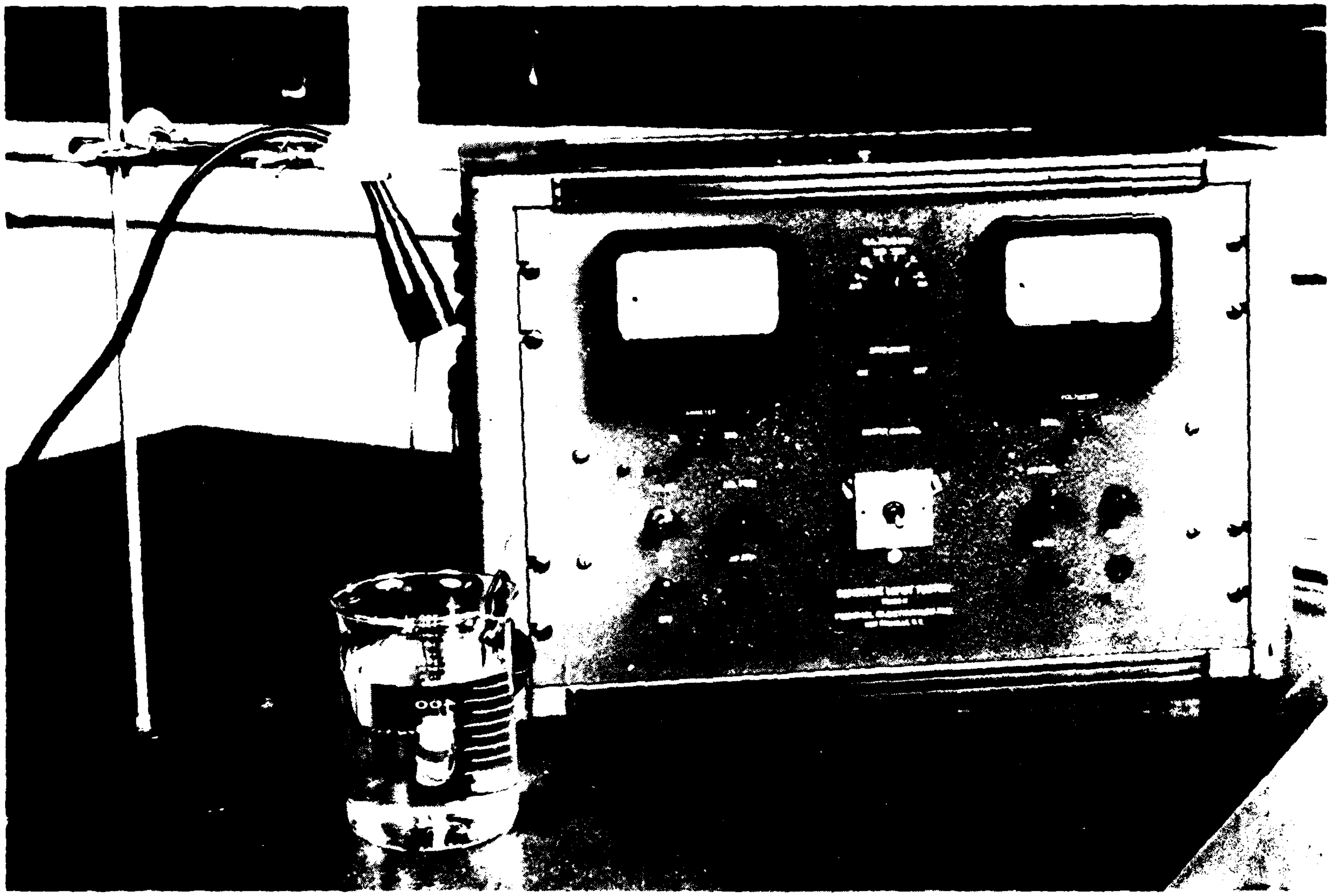

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Figure 3. Hypot proof testing of a wire specimen.

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Figure 4. Failed wire specimens. The wires were wrapped around ½-inch diameter Teflon rods prior to water aging.

The exposure test cycles were established by a pre-data run with two specimens aged at 80°C and 100°C to obtain an approximation of life at these temperatures. Where practical each cycle period was established to approximate one-tenth of the estimated lifetime, except for the 100°C aging where the minimum timing of 24 hours was applied. These aging schedules were as follows:

Water Temperature:	100°C	80°C	60°C
Hours Per Cycle:	24	48	72

Failures did not all occur at the same cycle, so the failure times of the ten specimens at each aging temperature were averaged to determine the life at that temperature. Time to failure of a specimen was determined by taking the total exposure time of the cycles through which it passed the proof-test plus one-half of the time of the last cycle. The time for each data point on the Arrhenius plot is the log average life of the ten specimens tested at that temperature.

$$\text{Log average life} = \log \frac{\log t_1 + \log t_2 + \log t_3 \; . \; . \; . \; . + \log t_{10}}{10}$$

where t_1, t_2, t_3, ... t_{10} are the successive times to failure of the 10 specimens of that group.

It would be possible to make a complete regression analysis of the life-temperature data thus obtained by following the statistical analysis procedure in IEEE Standard No. 101. However, the abbreviated procedure of this standard was applied here to plot the best-fit straight line to the data points.

The Arrhenius plots of each wire sample are shown in Figures 5 and 6 showing the data spread of the ten specimens at each temperature point and the close fit of the log average life points to a straight line. A plot of the two samples studies is presented in Figure 7, showing that the slopes are nearly the same, indicating that the activation energy for the hydrolytic degradation mechanism is the same for each sample. Since the lines do not overlap, variations in the wire manufacturing process are attributed to the shift in the constant of the Arrhenius equation.

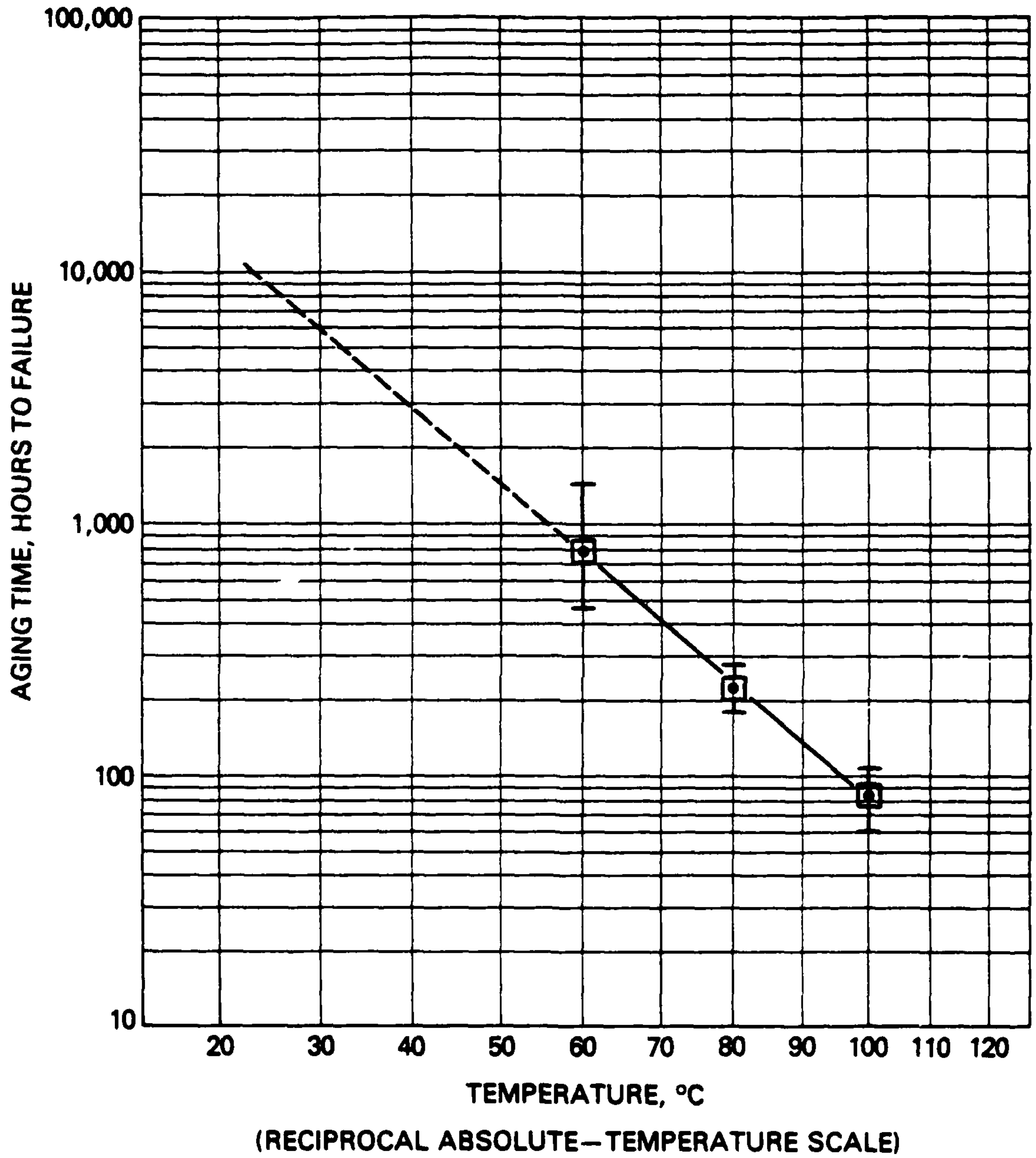

Figure 5. Life versus water aging temperature of wire sample no. 1, MIL-W-81381/11, AWG 22, aromatic polyimide (Kapton®) insulation.

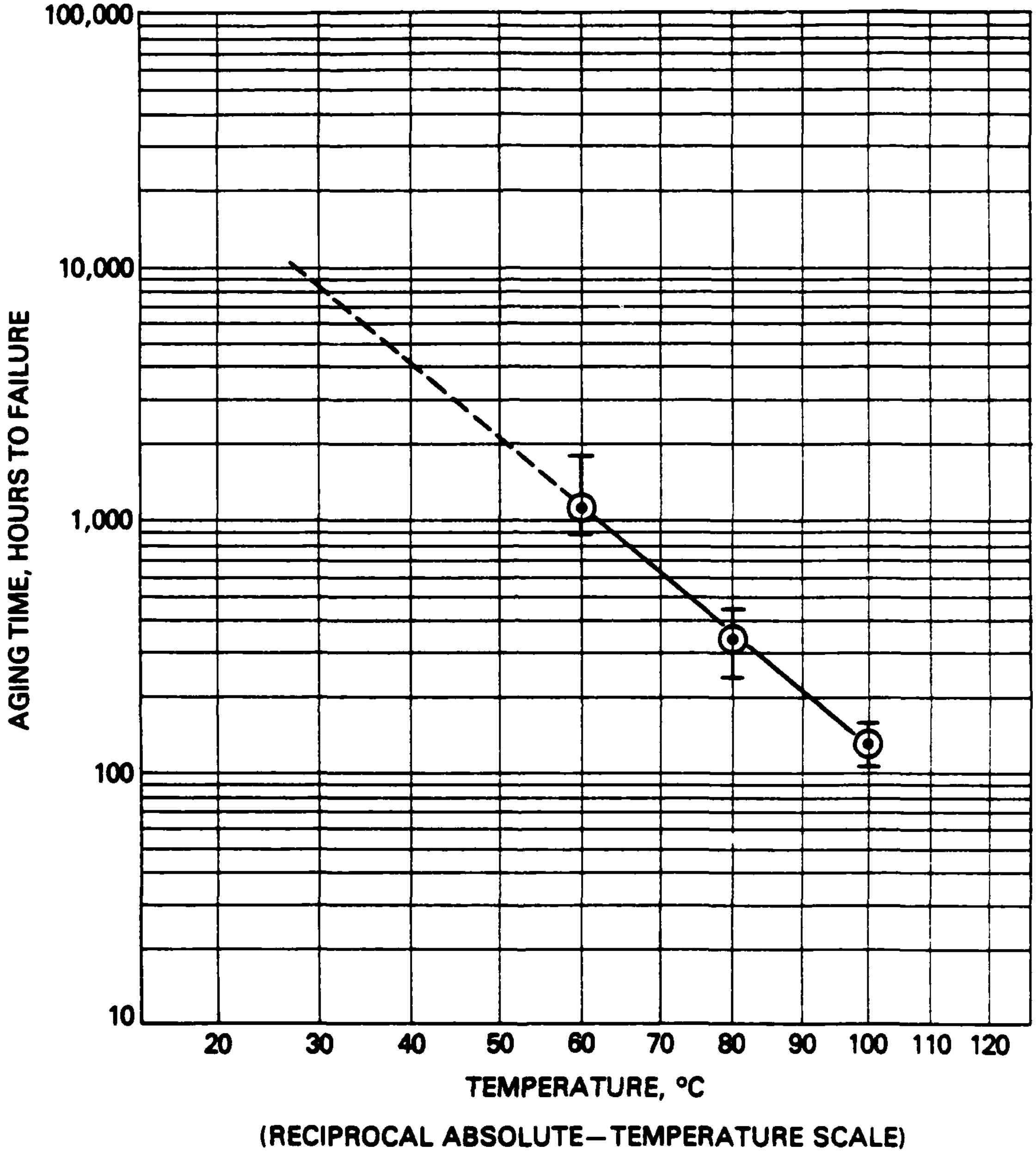

Figure 6. Life versus water aging temperature of wire sample no. 2, MIL-W-81381/11, AWG 22, aromatic polyimide (Kapton®) insulation.

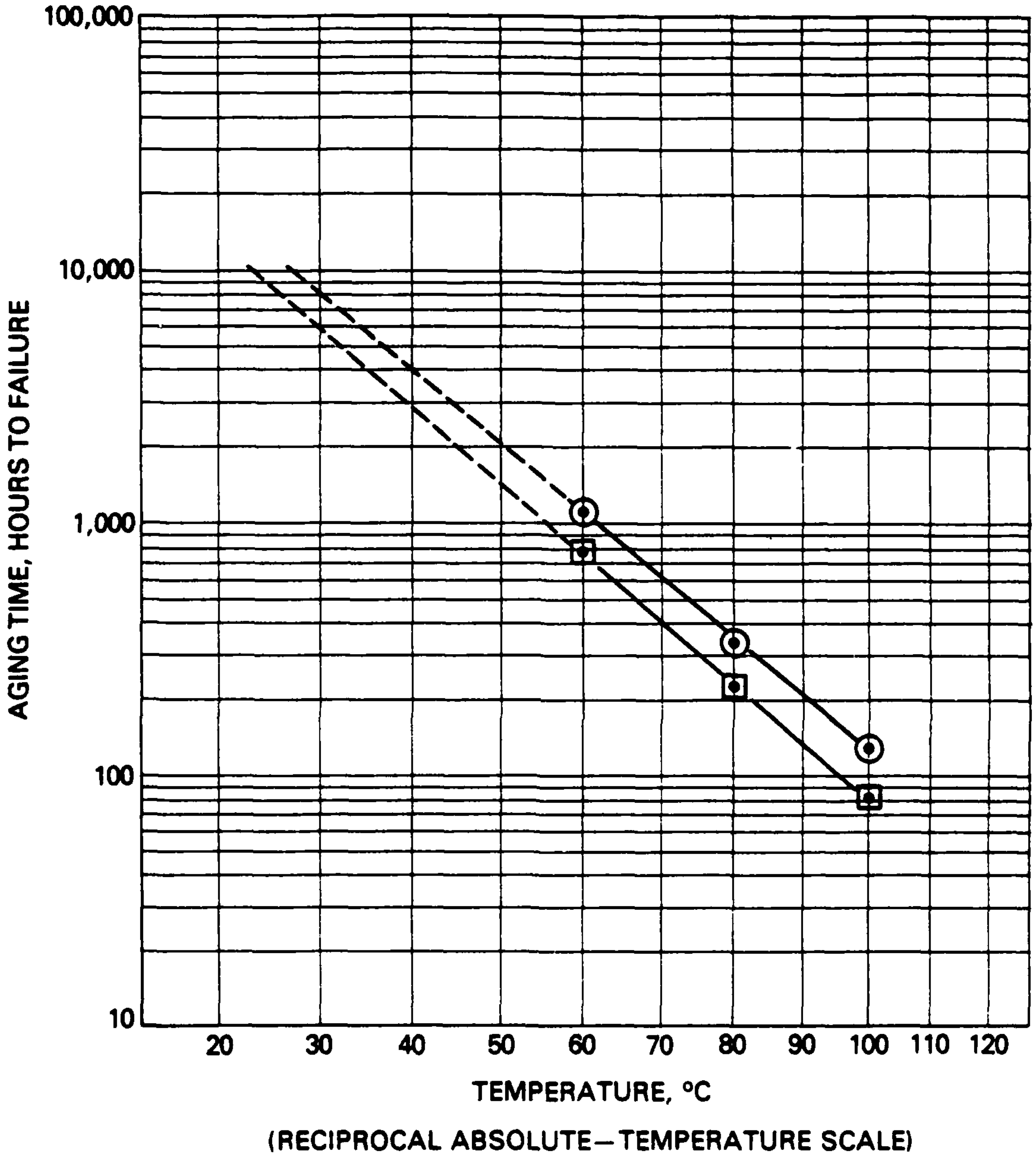

Figure 7. Comparison of Arrhenius plots of wire samples from two different manufacturers. MIL-W-81381/11, AWG 22, aromatic polyimide (Kapton®) insulation.

CONCLUSIONS AND RECOMMENDATIONS

The results of this initial experiment demonstrate that the Arrhenius rate equation can be applied to achieve linear extrapolation from higher temperature, shorter life tests in order to approximate the lifetime of the insulation system at the service temperature under the same conditions of aging. Other parameters of stress held constant throughout the test will have an effect on the intercepts (predicted life at a specified service temperature), but manufacturing variations in which the same materials were used will probably not affect the slope. For example, wrapping the wires on a smaller diameter rod will impose a greater stress on the outer perimeter of the insulation and thus reduce the time to failure at the test temperature. Since other studies found in the reference literature confirm that the major reaction in Kapton® degradation is chain splitting by hydrolysis, the same procedure of accelerated testing should also be applicable to other variations in the nature of the aqueous media of the aging exposure test. Typical high humidity conditions of the aircraft carrier can also produce the hydrolysis reaction, and thus life in a humid environment should also be predictable by extrapolating from accelerated temperature tests in controlled humidity chambers by the Arrhenius plot procedure. Further studies will be conducted to determine if this can be applied by substituting controlled humidity exposures in place of the deionized water of this first study.

The long-range program objective does not only address this specific problem of determining the effects of hydrolysis in service-simulated aqueous exposures on the service life of this one type of insulation used on Navy aircraft. The selection of alternative types is now also an important policy course to be followed in future aircraft wiring installations. Other

insulation systems may be less vulnerable to hydrolytic degradation, but may be more adversely affected by other service environments or stresses. Thus, a functional aging procedure which incorporates these other possible major stress parameters in a multi-factor accelerated process will be developed in order to obtain an estimation of service life and a comparison of insulation systems.

In addition, the Arrhenius plot provides a relative comparison of various manufacturers' experimental wire insulation products so that the same procedures will provide an index of quality that is useful to industrial laboratories. Therefore, the procedure will be an essential addition to the other quality assurance and performance requirements of the existing wire specification documents.

REFERENCES

1. NARF Report No. 03-76, Fluid Immersion Testing of Electrical Wire, North Island Rework Facility, February 13, 1976.
2. NADC Report, "Airframe Wire Evaluation: Resistance to Heat and Aircraft Surface Cleaners (MIL-C-43616)", Naval Air Development Center, June 5, 1978.
3. Sandia Report SC-TM-70-228, "Effects of Humidity on Polyimide-Insulated Cables Used on the W-68", Sandia Laboratories, April 1970.
4. R. DeIasi and J. Russell, "Aqueous Degradation of Polyimides", Journal of Applied Polymer Science, Vol 15, pp 2965-2974 (1971).
5. F.J. Campbell and E.L. Brancato, "Determination and Application of Thermal-Life Characteristics of Aerospace Wires", Insulation, Part 1 pp 17-22, October 1963; Part 2 pp 23-30, November 1963.
6. D.K. Elliot, "A Standardized Procedure for Evaluating the Relative Thermal Life and Temperature Rating of Thin-Wall Airframe Wire Insulation", IEEE Transactions on Electrical Insulation, Vol EI-7, No. 1, pp 16-25, March 1972.
7. ASTM Standard No. D 3032-82, Section 14, "Standard Method of Testing Hookup Wire Insulation for Relative Thermal Life and Temperature Index"
8. T.W. Dakin, "Electrical Insulation Deterioration Treated as a Chemical Rate Phenomena", AIEE Transactions, Vol 67, pp 113-122, 1948.